Time- and Space-Resolved Spectroscopic Investigation on π-Conjugated Nanostructures

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Table of Contents

Abstract

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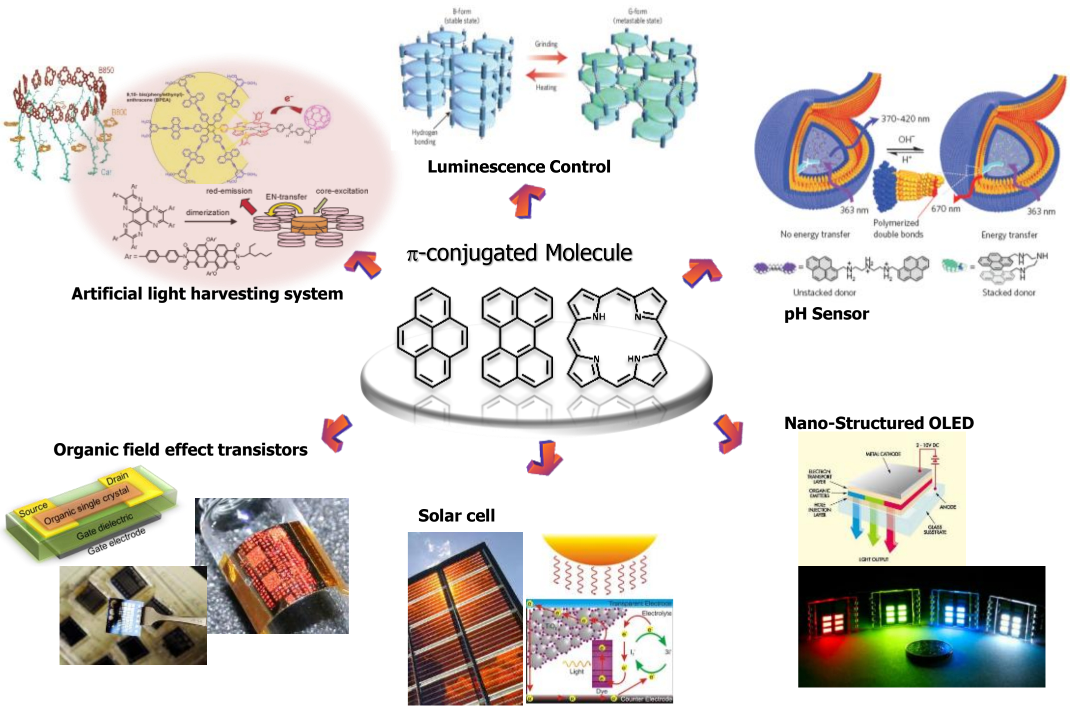


Figure 1. Various applications of π-conjugated molecular systems

Introduction

Over the past few decades, researchers have witnessed a rapid growth in the applications of π-conjugated nanostructured organic materials. This fact has inspired numerous research activities ranging from fundamental studies of their chemical versatility and photophysical properties to practical applications such as molecular photonic devices, artificial photosynthesis systems, and dye-sensitized solar cells. Strenuous research efforts have focused on developing new types of π-conjugated organic molecules that display certain characteristics for applications. In this context, a detailed understanding of the relationship between structure and photophysical properties in crucial for the fabrication of novel π-conjugated systems targeted for specific application.

In the study of functional π-electronic molecular systems, we focus on the π-conjugation pathways and π-π interactions. First, the π-conjugation pathway is directly related to the topologies and the number of π-electrons of π-conjugated molecules. Particularly, a control of conformational flexibility is critical in determining the π-conjugation pathway. In this regard, compared with normal all-carbon annulene molecules, expanded porphyrins are best candidates to investigate the structure/property relationship in view of aromaticity and an index for π-conjugation, because a comparable set of [4n] / [4n+2] expanded porphyrin can be systematically prepared due to an easy two-electron oxidation/reduction of pyrroles

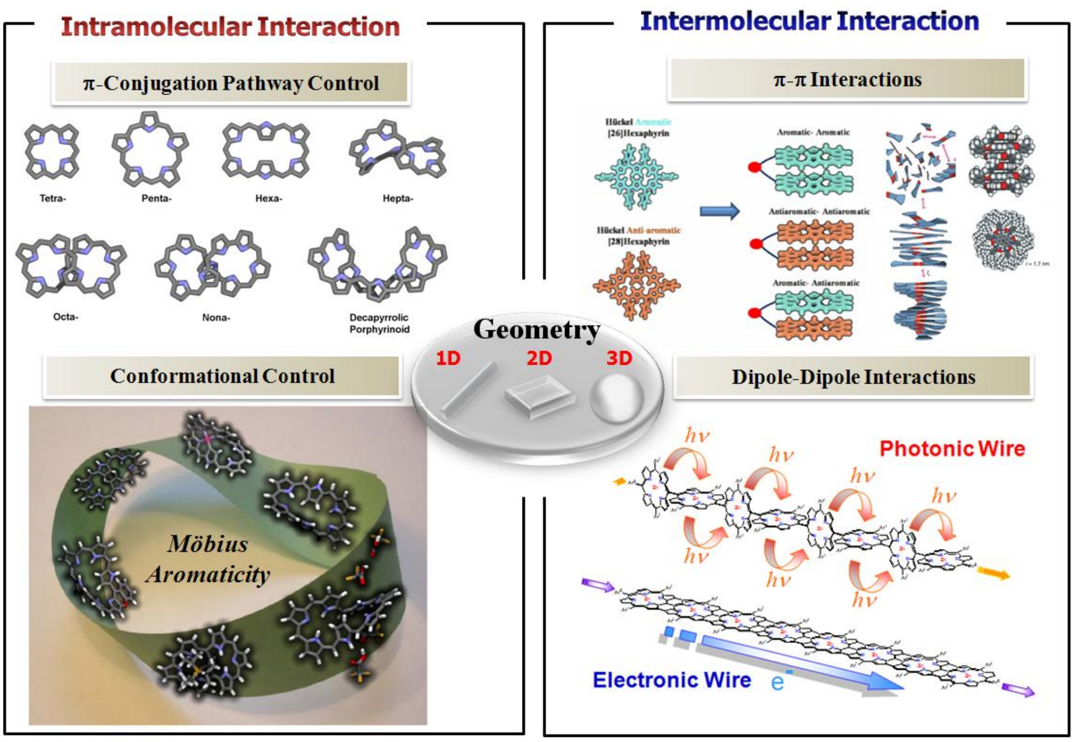


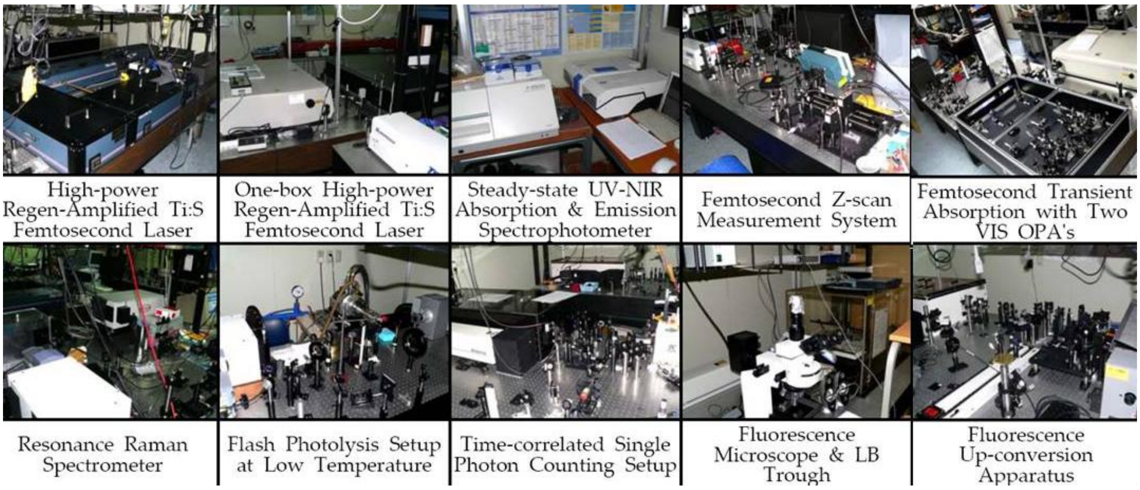
Figure 2. Research contents for functional π-electronic molecular systems

through a stepwise addition of pyrrole rings into the tetrapyrrolic porphyrin macrocycle. Furthermore, by controlling π-conjugation pathway through changing the constituent moieties and substituents, some π-conjugated molecules can obtain biradical character in ground state, which is unusual phenomenon, leading totally different photophysical properties as compared to others. Through time-resolved transient absorption and two photon absorption spectroscopy, we unveil the electronic structures of π-conjugated molecular systems in relation to the modification of π-conjugation pathway. Another important issue in π-electronic molecular systems is π-π interactions in various molecular architectures such as liquid crystals, supramolecules, molecular aggregates, nanofibers, and so on. In the formation of such molecular structures, the π-π stacking plays a crucial role by providing intermolecular interaction forces between constituent molecular elements. Depending on the distance and orientation between the adjacent constituent molecules as well as π-conjugation associated with molecular topologies, π-π stacking interactions would be different, leading to versatile molecular architectures. Thus we investigate the extent of π-π electronic interactions in these systems by using time-resolved transient absorption and polarization anisotropy spectroscopy.

Consequently, with active control of π-conjugation and π-π interaction, this work has explored the structure-property relationship of various π-conjugated molecular systems in conjunction with aromaticity, biradical and energy diffusion processes by using ultrafast spectroscopic measurements as well as theoretical calculations.

Experiment

(1) Experimental Method



① **Steady-State Laser Spectroscopy**

•Laser-Induced Luminescence Spectroscopy

② **Time-Resolved Laser Spectroscopy**

•Nanosecond Flash Photolysis

•Picosecond Time-Correlated Single Photon Counting (TCSPC) Method

•Vis/IR Femtosecond Transient Absorption Spectroscopy

•Femtosecond Fluorescence Up-Conversion Spectroscopy

③ **Non-Linear Spectroscopy**

•Femtosecond Z-Scan Method

(2) Quantum Mechanical Calculation

• Nuclear-Independent Chemical Shift (**NICS**) Values

• Anisotropy of the Induced Current Density (**AICD**) Calculation

• Molecular Orbitals & Electronic Excited-State Excitation Energies

Results and Discussion

1. Deprotonation-Induced Aromaticity Enhancement and New Conjugated Networks in *meso*-Hexakis(pentafluorophenyl)[26]hexaphyrin

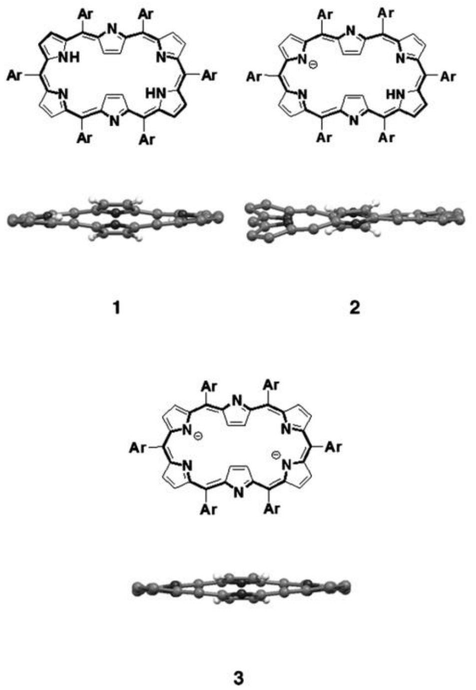


Figure 3 Molecular structures of [26]hexaphyrin free-base **1**, monoanion **2**, and dianion **3**.

meso-Hexakis(pentafluorophenyl)-substituted neutral hexaphyrin with a 26π-electronic circuit can be regarded as a real homolog of porphyrin with an 18π -electronic circuit with respect to a quite flat molecular structure and strong aromaticity. We have investigated additional aromaticity enhancement of *meso*-hexakis (pentafluorophenyl) [26] hexaphyrin(1.1.1.1.1.1) by deprotonation of the inner NH groups in the macrocyclic molecular cavity to try to induce further structural planarization (Figure 3). Deprotonated mono- and dianions of [26] hexaphyrin display sharp B-like bands, remarkably strong fluorescence, and long-lived singlet and triplet excited-states, which indicate enhanced aromaticity (Figure 4). Structural, spectroscopic, and computational studies have revealed that deprotonation induces structural deformations, which lead to a change in the main conjugated p-electronic circuit and cause enhanced aromaticity. Also, we examined the singlet and triplet excited state lifetimes of **1**, **2**, and **3** by transient absorption (TA) measurements (Figure 5). While the S_1 state lifetime of **1** was recorded to be 103 ps in toluene by femtosecond time-resolved TA

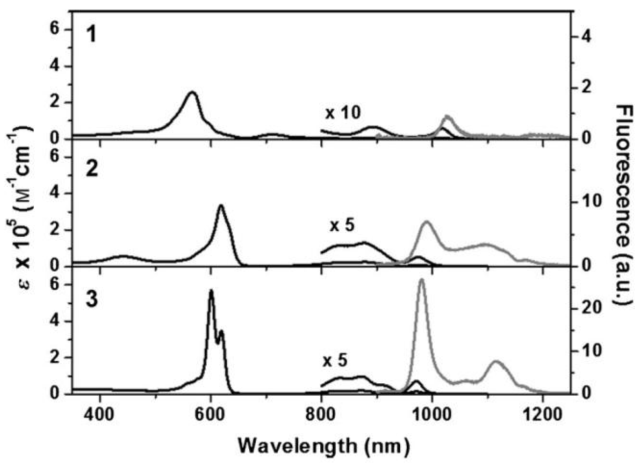


Figure 4 Steady-state absorption (black line) and fluorescence (gray line) spectra of **1**, **2**, and **3** in CH_2Cl_2.

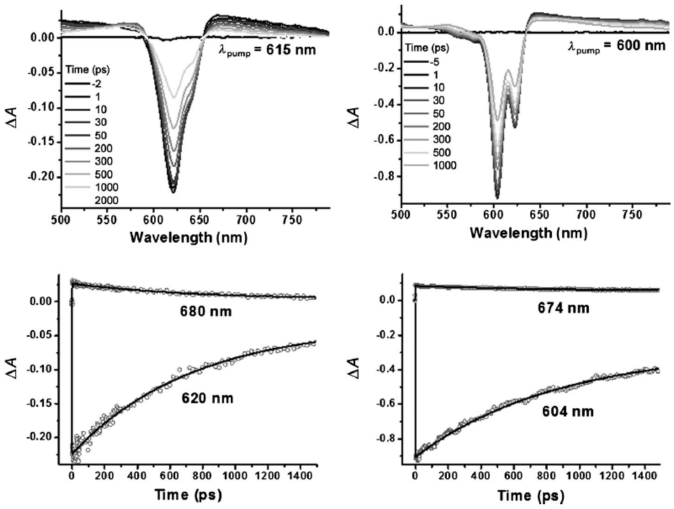


Figure 5 TA spectra and decay profiles of **2** (left) and **3** (right) in toluene.

spectroscopy, those of monoanion and dianion were much longer: 740 and 870 ps, respectively. The long-lived S_1 states and increased fluorescence intensities of **2** and **3** compared with **1** suggest that the nonradiative rates in the S_1 states of **2** and **3** substantially decrease with respect to the radiative rate constants. By means of the nanosecond time-resolved flash photolysis technique, the triplet excited-state lifetimes of **2** and **3** were determined to be 10.4 and 22 ms, respectively. Thus, it may be concluded that deprotonation leads to long-lived lifetimes for both the singlet and triplet excited states. And the four frontier molecular orbitals (HOMO-1, HOMO, LUMO, and LUMO+1) play an important role in determining the photophysical properties of expanded porphyrins. Interestingly, the HOMO–LUMO energy gaps of **1**, **2**, and **3** are almost equal to 1.80 eV and the LUMO and LUMO+1 of **3** become nearly degenerate with a very small energy difference of 0.017 eV. Compared with **1**, deprotonated species **2** and **3** exhibit more degenerate LUMO and LUMO+1 orbitals which are similar to typical aromatic porphyrinoid systems following Gouterman's four-orbital model. In conclusion, Hexaphyrin undergoes facile deprotonation upon treatment with Tetrabutylammonium Fluoride (TBAF) to generate monoanion and dianion, both of which display sharp absorption spectra, exceptionally increased fluorescence intensities, and considerably long-lived singlet and triplet excited states as an indication of enhanced aromaticity. This work highlights the potential of the deprotonation strategy for tuning the electronic properties of expanded porphyrins. Hence, applications of this strategy to larger expanded porphyrins are actively being pursued in our laboratories.

2. An Electron-Deficient Porphyrin Tape

Recently, by combining electron-rich- and electron-poor porphyrins, we have developed hybrid porphyrin tapes with improved solubility and chemical stability compared with their parent porphyrin tapes. As an extension of this strategy, herein we report the synthesis and characterization of an electron-deficient triply linked porphyrin tape that consists of only

pentafluorophenyl-substituted Zn^{II}–porphyrin units. This structure was used to examine the influence of the electron-deficient substituents on the stability, solubility, and electronic properties of porphyrin tapes.

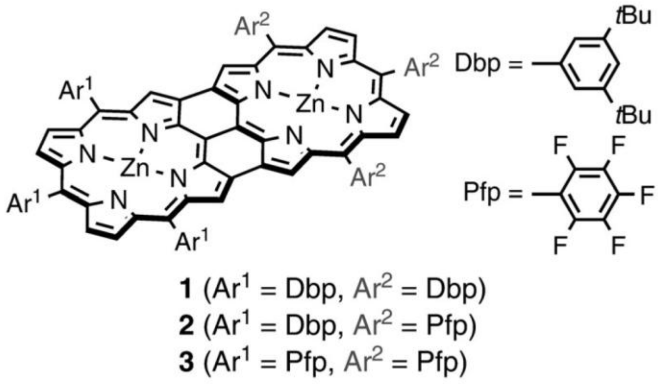


Figure 6 Structures of meso-meso,β-β,β-β triply linked diporphyrins **1**–**3**

Beside the red-shifted absorption spectrum and split first oxidation potential that are common to the triply-linked Zn^{II}–diporphyrins, diporphyrin **3** exhibited considerably improved chemical stability owing to a lowered HOMO and good solubility in common organic solvents. The two-photon absorption (TPA) cross-section and S_1-state lifetime of compound **3** were 1700 GM and 3.3 ps, respectively.

Extensive studies were carried out to elucidate the molecular structure – TPA property relationship. The most important factor for the enhancement of TPA was presumably the extension of π-electron conjugation. Another effective factor that was proposed to enhance TPA was charge-transfer interactions. In this context, meso-meso, β-β, β-β triply linked diporphyrins **1**–**3**, which could be regarded as D-D, D-A, and A-A (D: a 3,5-di-tert-butylphenyl-substituted donor-type porphyrin, and A: a pentafluorophenyl-substituted acceptor-type porphyrin), respectively, were used to examine the effects of charge-transfer interactions on TPA property. In compounds singly linked Zn^{II}–diporphyrin **9** and **3**, the maximum TPA cross-sections were 240 and 1700 GM, respectively; the TPA value per porphyrin units (σ^2/N) of compound **3** was about seven times larger than that of compound **9**, thus showing that the TPA values were strongly associated

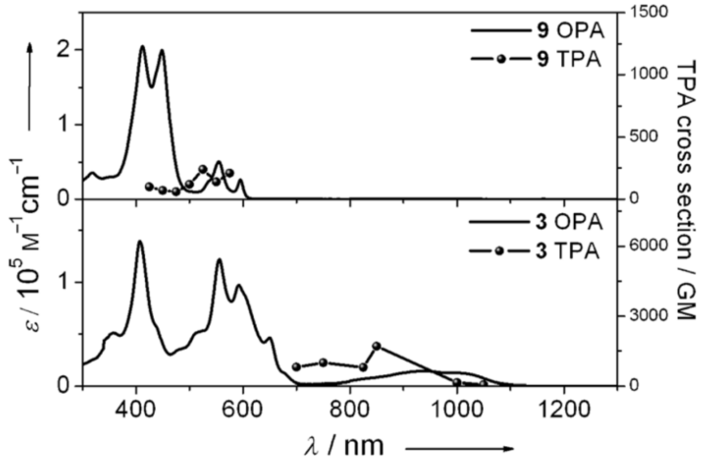


Figure 7 One- (OPA) and two-photon absorption (TPA) spectra of compounds **9** (top) and **3** (bottom) in CH_2Cl_2. TPA spectra are plotted at λex/2.

with effective p-conjugation. Compared with **1** and **2**, the TPA values of **3** were relatively small. Seemingly, the D-D and D-A structures were more effective at enhancing TPA property than the A-A system and charge-transfer interaction played some role in TPA enhancement.

3. Kinetically Blocked Stable Heptazethrene and Octazethrene: Closed-Shell or Open-Shell in the Ground State?

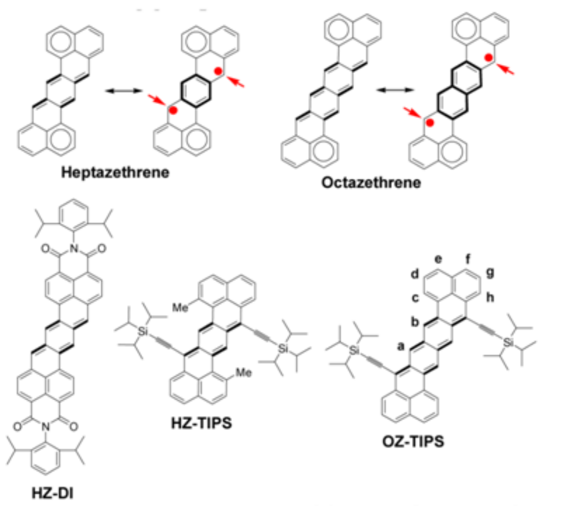


Figure 8 Resonance Structures of Heptazethrene and Octazethrene and Structures of HZ-TIPS and OZ-TIPS

In this paper, we report an efficient synthetic route for a new kinetically blocked heptazethrene derivative (HZ-TIPS), in which the most reactive sites (indicated by arrows in Figure 8) are substituted by bulky triisopropylsilylacetylene (TIPS) groups (Figure 8). By using a similar concept, the first stable octazethrene derivative (OZTIPS, Figure 8), which was found to have a singlet open-shell ground state, was also obtained. The ground-state electronic structures of both compounds were systematically studied by a combination of different experimental methods, including steady-state and transient absorption spectroscopy, variable temperature nuclear magnetic resonance (NMR), electron spin resonance (ESR), superconducting quantum interfering device (SQUID), FT Raman, and X-ray crystallographic analysis, assisted by unrestricted symmetry-broken density functional theory (DFT) calculations. Their non-linear optical (NLO) properties and solid-state packing were also investigated in detail.

We have found that the third-order NLO response generally reflects variations in the electronic structure as well as the conformational geometry of the molecules, giving rise to the underlying static and dynamic polarizability.

In contrast with HZ-TIPS, OZ-TIPS has an unusual ground-state structure with an open-shell configuration, which should be one of the most attractive issues in understanding the TPA−structure correlation between these derivatives. The large TPA activities of bis(phenalenyl) hydrocarbons with benzene and naphthalene spacers possessing an intermediate singlet biradical character have been reported. To characterize NLO properties,

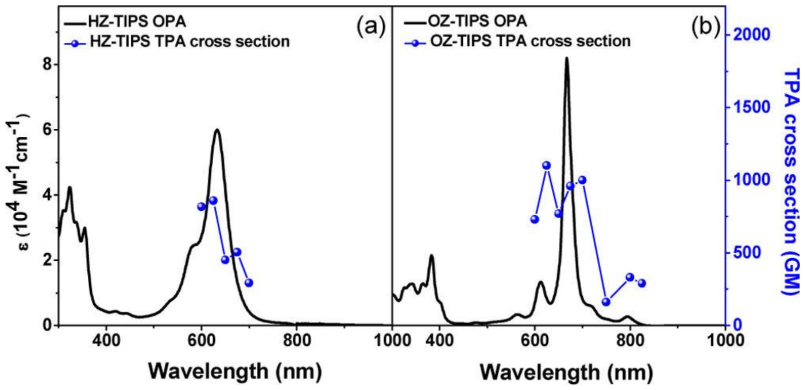


Figure 9 OPA (black solid line and left vertical axis) and TPA spectra (blue symbols and right vertical axis) of (a) HZ-TIPS and (b) OZTIPS in chloroform. TPA spectra are plotted at λex/2.

the TPA values of HZ-TIPS and OZ-TIPS were measured by using a wavelength-scanning open aperture Z-scan method in the wavelength range from 1200 to 1650 nm, where one-photon absorption contribution is negligible. In relevance to the structure-correlation of radical character, while the TPA cross-section of the closed-shell system HZ-TIPS was determined to be 920 GM at 1250 nm, OZ-TIPS possessing a singlet biradical character exhibited an enhancement of TPA cross section value of 1200 GM at 1250 nm. Such an enhancement on the third-order NLO property can be explained by the larger singlet biradical character of OZ-TIPS.

Both compounds show large TPA cross sections, which is in agreement with theoretical predictions on the open shell singlet biradicaloids. The large TPA response and good stability of these new compounds indicate their potential applications in nonlinear optics. By collecting all these experimental data and theoretical calculations, a clear picture of the ground state structure can be figured out: HZ-TIPS has a closed-shell ground state while the higher order OZ-TIPS has an open-shell singlet biradical ground state. Remarkably, the singlet biradical character y = 0.56 for OZ-TIPS was obtained by a combination of the OPA, TPA, and SQUID data.

It is noteworthy that the first stable octazethrene derivative OZ-TIPS was synthesized, which has been pursued by chemists for a long time. The design concept and the new synthetic strategy starting from the corresponding diketone likely can be applied to the synthesis of other stable open-shell polycyclic hydrocarbons or hybrid structures.

4. Stable Tetrabenzo-Chichibabin's Hydrocarbons: Tunable Ground state and Unusual Transition between Their Closed-Shell and Open-Shell Resonance Forms

Chichibabin's hydrocarbon as a classical open-shell PAH has been investigated for a long time. However, most of the studies are complicated by their inherent high reactivity. In this work, two new stable tetrabenzo-Chichibabin's hydrocarbons were synthesized by a new

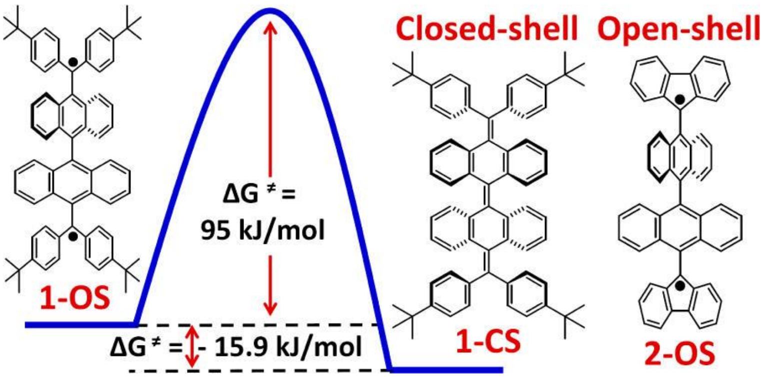


Figure 10 schematic energy diagram for tetrabenzo-Chichibabin's hydrocarbons

strategy, and their electronic structures and geometries in the ground state were investigated by various experiments assisted by quantum mechanical calculations. Their ground-state structures were tunable, with **1-CS** as a closed-shell hydrocarbon and **2-OS** as an open-shell biradical. Such a difference can be explained by an enhanced thermodynamic stabilization of the biradicaloid resonance form when the di(4-tert-butylphenyl)methene groups in **1-CS** were replaced by fluorenyl units in **2-OS**. The extremely high stability of the biradical **2-OS** can be ascribed to thermodynamic stabilization by delocalization and kinetic blocking by the anthracene units. Their excited states were also approachable by chemical means, and an unusually slow transition from the orthogonal **1-OS** to a highly contorted butterfly like **1-CS** was observed, which can be explained by a very large energy barrier arising from steric repulsion during the transition. A quinoidal form **2-CS** represented the excited state of **2-OS**, and it quickly relaxed back to the ground state during chemical synthesis. The nature of the biradical in **2-OS** was confirmed as two weakly coupled radicals with a triplet ground state and a small singlet−triplet energy gap (ΔE_{S-T} = −1.4 kJ/mol). Both compounds can be oxidized into stable dications by chemical oxidation. FT Raman spectroscopy also provided further structural information, such as a quinoidal form for **1-CS** and a benzenoid form for **2-OS**, **1-CS^{2+}**, and **2-OS^{2+}**, which was consistent with other experimental data. The open-shell **2-OS** has a shorter singlet excited state lifetime than that of closed-shell **1-OS**,

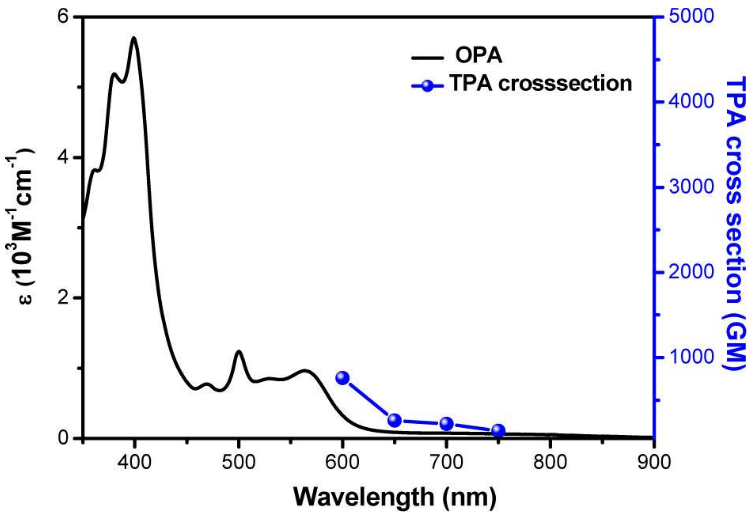


Figure 11 OPA (black solid line and left vertical axis) and TPA spectra (blue symbols and right vertical axis) of 2-OS in chloroform. TPA spectra were plotted at λex/2.

which can be considered to reflect a radical-induced acceleration of the nonradiative internal conversion rates. Moreover, to investigate the NLO properties of the biradical **2-OS**, two-photon absorption measurements were conducted by using the open-aperture Z-scan method with 130 fs pulses in the NIR region from 1200 to 1500 nm where one-photon absorption (OPA) contribution is negligible. As shown in Figure 10, although **2-OS** had a rather small OPA absorption coefficient, it showed a large TPA cross section in the wavelength region with the maximum value as 760 GM at 1200 nm. In comparison with typical hydrocarbon chromophores, which only exhibited a small TPA value at the long wavelength, a relatively larger cross section for compound **2-OS** was obtained, and was comparable to the achieved value of other open-shell PAH molecules (300−890 GM) in the same region of photoexcitation. This result can be reasonably understood by the unusual ground-state electronic structure of **2-OS** with distinct biradical character. The measurement on the closed-shell **1-CS** however was limited by its too short absorption wavelength, which was out of the range of the photoexcitation wavelength of our facilities. That is indicating promising potential applications of open-shell PAHs in nonlinear optics. Chichibabin's hydrocarbon **2-CS**/**2-OS** provides a new candidate for a study on charged antiaromatic species.

5. Exciton delocalization and dynamics in helical π-stacks of self-assembled perylene bisimides

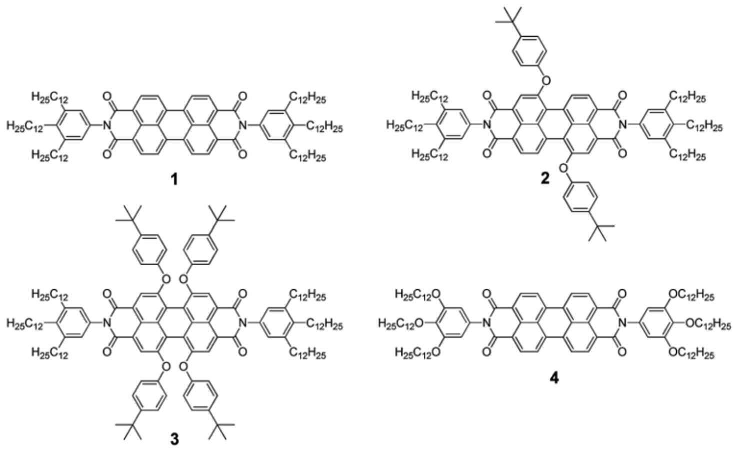


Figure 12 Molecular structures of PBI dyes employed in this study. PBIs **1** and **4** adopt helical aggregate structures in MCH solvent at high concentrations while PBIs **2** and **3** have dimer and monomer forms, respectively. PBI **4** with its electron-donating 3,4,5-tridodecyloxyphenyl substituents shows non-fluorescence behavior.

Whilst the excitonic properties of J-aggregates have been investigated in great detail, those of H-aggregates have not been systematically investigated yet. In this regard, we have explored the exciton dynamics and excited-species formation processes in columnar H-aggregates of planar PBI dyes that are stacked in a helical fashion by various spectroscopic techniques such as time correlated single-photon

counting (TCSPC) and femtosecond pump–probe measurements with anisotropy changes. The outcome of this study is that photogenerated excitons in helically stacked PBI dyes experience complicated relaxation processes that involve excited-state interactions such as exciton delocalization and excimer formation.

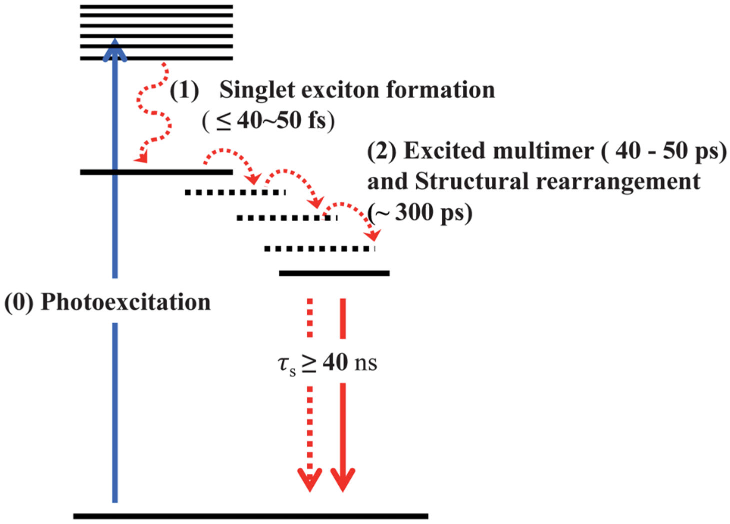


Figure 13 Exciton dynamics in helically stacked aggregates of PBI dyes.

To scrutinize the exciton dynamics in the helically stacked aggregates, we have also ㆆ included PBI **2** and **3**, distorted bay-substituted PBI dyes as reference molecules. PBI **2** exhibit only relatively small-sized dimeric aggregate structures, whereas PBI **3** forms no multimeric structure at all. The comparative study revealed that the excited-state interactions in the large-sized helically stacked aggregates extend beyond two PBI units, leading to a final excimer (here, excimer means not only an “excited dimer” but an “excited multimer”) trap state within ~50 ps. Although in competition with this relaxation path into the excimeric trap state, exciton diffusion has been revealed by exciton–exciton annihilation processes, occurring at high excitation power. Whilst the excimer formation process interrupts the direct observation of exciton diffusion in these columnar PBI aggregates, the exciton migration distance could be estimated by the incorporation of non-fluorescent PBI **4** quencher molecules into PBI **1** aggregates. From this analysis we can conclude that the exciton diffusion can reach a length of about 10 monomer units. Although this value appears to be shorter than those values observed for J-aggregates, this result shows that columnar PBI stacks might still be useful for optoelectronic applications if the relaxation process leading to excimer traps is prevented, e.g. by structural modifications of the molecules.

Summary

In this project, we have investigated the photophysical properties of various π-electronic molecular systems, such as expanded porphyrins, fused porphyrin arrays, π-π stacked molecular molecular assemblies *etc*. by combining our integrated time-resolved spectroscopic methodologies.

Firstly, the aromaticity enhancement for [26]π hexaphyrins was investigated by deprotonation of the inner NH groups in the macrocyclic molecular cavity, which induce further structural planarization. Spectroscopic and computational studies have revealed that deprotonation leads structural deformation, which induce a change in the main π-conjugation pathway and cause enhanced aromaticity. Consequently, this work suggests the potential of the deprotonation strategy for tuning the electronic properties of expanded porphyrins. Secondly, nonlinear optical properties of expanded porphyrins and π-conjugated molecules having biradical character are investigated through the measurement of TPA cross section. The TPA values of fused porphyrin tapes can be increased by charge-transfer interaction between porphyrin backbone and electron donor or acceptor. Furthermore, stable biradicaloids perturbs the electronic structure as well as the conformational geometry, giving rise to the enhancement of TPA cross section. Lastly, the exciton dynamics in H-aggregates are systematically investigated in columnar aggregates of planar PRI molecules by TCSPC and femtosecond pump-probe measurements with anisotropy changes. The experimental results suggest that columnar PBI stacks can be useful for optoelectronic applications if the relaxation process leading to excimer traps is prevented by structural modifications of the molecules.

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1. Kinetically Blocked Stable Heptazethrene and Octazethrene: Closed-Shell or Open-Shell in the Ground State?

Yuan Li, Wee-Kuan Heng, Byung Sun Lee, Naoki Aratani, JoséL. Zafra, Nina Bao, Richmond Lee, Young Mo Sung, Zhe Sun, Kuo-Wei Huang, Richard D. Webster, Juan T. López Navarrete, Dongho Kim, Atsuhiro Osuka, Juan Casado, Jun Ding, Jishan Wu

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2. Stable Tetrabenzo-Chichibabin's Hydrocarbons: Tunable Ground State and Unusual Transition between Their Closed-Shell and Open-Shell Resonance Forms

Zebing Zeng, Young Mo Sung, Nina Bao, Davin Tan, Richmond Lee, José L. Zafra, Byung Sun Lee, Masatoshi Ishida, Jun Ding, Juan T. López Navarrete, Yuan Li, Wangdong Zeng, Dongho Kim, Kuo-Wei Huang, Richard D. Webster, Juan Casado, Jishan Wu

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3. An Electron-Deficient Porphyrin Tape

Hirotaka Mori, Takayuki Tanaka, Naoki Aratani, Byung Sun Lee, Pyosang Kim, Dongho Kim, Atsuhiro Osuka

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4. Excitation energy migration processes in various multi-porphyrin assemblies

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5. Tetrakis(4-tert-butylphenyl) substituted and fused quinoidal porphyrins

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6. A non-fused mono-meso-free pentaphyrin and its rhodium(I) complex

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7. Deprotonation-Induced Aromaticity Enhancement and New Conjugated Networks in meso-Hexakis(pentafluorophenyl)[26]hexaphyrin

Won-Young Cha, Jong Min Lim, Min-Chul Yoon, Young Mo Sung, Byung Sun Lee, Sho Katsumata, Masaaki Suzuki, Hirotaka Mori, Yoshiya Ikawa, Hiroyuki Furuta, Atsuhiro Osuka, Dongho Kim

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8. Exciton delocalization and dynamics in helical π-stacks of self-assembled perylene bisimides

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9. Functionalization of Hexa-peri-hexabenzocoronenes: Investigation of the Substituent Effects on a Superbenzene

Ryuichi Yamaguchi, Satoru Ito, Byung Sun Lee, Satoru Hiroto, Dongho Kim, Hiroshi Shinokubo

Chem. Asian J. **2013**, *8*, 178 – 190

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